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On Mercurous Nitrite.—By P. C. RÂÏ, D. Sc.

(Read December, 1895.)

Preliminary.

Having recently had occasion to prepare mercurous nitrate in quantity by the action of dilute nitric acid in the cold on mercury, I was rather struck by the appearance of a yellow crystalline deposit. At first sight it was taken to be a basic salt, but the formation of such a salt in a strongly acid solution was contrary to ordinary experience. A preliminary test proved it, however, to be at once a mercurous salt as well as a *nitrite*. The interesting compound promised thus amply to repay an investigation.

Historical.

Lefort, Gerhardt and Marignac, especially the last, have studied and described in detail the action of nitric acid on mercury under varying circumstances. We have to labour here under the serious disadvantage of not having access to the original memoirs of these French chemists. Fortunately, a complete resumé of Marignac's work is to be found in Fremy's *Encyclopédie Chimique*. The information as regards mercurous nitrite, however, is scarcely worth anything.* Roscoe and

* The words which have a direct bearing on the present subject are quoted here: "L'azotite mercureux se forme .. en meme temps que l'azotate mercurique, d'après Lefort, chaque fois que l'on attaque du mercure par de l'acide nitrique. D'autre part, Gerhardt n'admet pas l'existence de l'azotite mercureux et il considère les produits obtenus comme de l'azotate mercurioso-mercurique." Tome III., p 240.

Schorlemmer in their well-known treatise do not so much as mention this compound, nor is there any reference to it to be found in the latest edition of Watt's *Dictionary of Chemistry*.

Method of Preparation.

Yellow nitric acid, sp. gr. 1.410, is diluted with water in the proportion of 1 to 3 in a flask or beaker. A large excess of mercury is at once poured into the liquid. The heat of solution of the acid in water helps to start the reaction. A gentle effervescence of gases at once takes place, and in the course of about an hour yellow needles, resembling prismatic sulphur, begin to appear on the surface of mercury. After a few hours the liquid together with the mercury is carefully decanted off, and the salt shaken out of the vessel over porous tiles to remove the adhering mother-liquor.

For purposes of analysis, *etc.*, it is preferable to collect the first day's or at most the second day's crops only, partly because minute globules of mercury get entangled among the mass of the crystalline deposit, which it is tedious to get rid of, and partly because the composition of the salt varies on standing in the liquid. Thus it is found that if the salt instead of being removed is allowed to remain in contact with the mercury and the mother-liquor, it gradually disappears and in its place transparent, perfectly colourless, crystals are formed, which grow in size with time. These latter will be described under the name of "Marignac's salt," which is a basic mercurous nitrate.

Qualitative tests.

The new compound among others answers to the following tests:—

1. Dilute sulphuric acid slowly evolves nitrous fumes: more readily on heating.

2. On warming with a large excess of water, globules of mercury separate out. In the cold the decomposition is only partial.

The *perfectly clear* mother-liquor, decanted off the mercury, gives the following reactions:—

(a) Boiled with an excess of pure caustic soda solution, it yields a black dense precipitate, the filtrate from which, after acidification with dilute sulphuric acid, rapidly decolorizes potassium permanganate solution and instantly sets free iodine from potassium iodide.

(b) Sodium chloride throws down a copious white precipitate; after removal of the calomel, the filtrate is now divided into several portions; to one is added caustic soda and a yellow precipitate is the result, another portion treated with potassium iodide gives an orange precipitate; whilst a third portion on addition of hydrochloric and phosphorous acids yields a further quantity of mercurous chloride.

It is thus evident that in the clear solution we have both a *mercurous* and a *mercuric* salt as well as a *nitrite*. Urea does not give the faintest opalescence to the liquid, showing the absence of *mercuric nitrate*.

QUANTITATIVE ANALYSIS.

A. *Estimation of Mercury.*

In determining the composition of the salt, the amount of mercury in it will have the predominating voice, on account of its high atomic weight; the nitrogen playing only a minor part. The estimation of this metal will therefore be described somewhat in detail.

It has already been shewn that when the salt is heated with a large bulk of water, metallic mercury separates out, leaving in solution both an *ous* and an *ic* salt. The mercury thus liberated sometimes collects readily into a single globule; sometimes it remains as a grey powder, the whole of which it is difficult to aggregate into globules, even after continued heating with hydrochloric acid. For estimation, the mercury is now transferred to a tared crucible and kept under a dessicator. The mercury weighed in this form will be termed "free" mercury all along.

The solution decanted off the mercury with the rinsings of the vessel is considerably diluted with water and an excess of hydrochloric and phosphorous acids added to it. The mixture is now allowed to stand overnight and the precipitate of mercurous chloride weighed in the usual way. When, however, it is desired to estimate the *ous* and the *ic* salts separately, treatment with sodium chloride is resorted to previous to the addition of hydrochloric and phosphorous acids, and the calomel then weighed in two instalments. Although this method yields accurate results, it often proves a very tedious one. After removal of the calomel by $\text{HCl} + \text{H}_3\text{PO}_3$, and further dilution of the filtrate with water, a small quantity of precipitate, varying from a few centi- to milligrams is generally obtained the succeeding day, and so on. Probably it was the nitrous acid necessarily present in the liquid which caused this kind of retardation in the precipitation of calomel.*

In a few cases the mercury in the *ic* salt was estimated as the *sulphide*. But this method is almost equally troublesome on account of the large quantity of sulphur set free. The pores of the filter-paper get choked up and the filtration, though carried on under reduced pressure with the aid of Bunsen's pump, proceeds very slowly. Moreover the precipitate has to be digested with a strong solution of sodium

* In the estimation of mercurous nitrate no such retardation occurs.

sulphite, thoroughly washed with hot water, dried and re-washed with carbon bisulphide, purified by being kept over mercury and re-distilled. Unless the precipitate is treated once more with carbon bisulphide, the result is apt to be too high. There is thus not much to choose between these methods. Both, however, give satisfactory results when conducted with care and patience.

Preparation I.—0.8695 gram. substance gave 0.274 gram. "free" mercury = 31.5 per cent. "free" mercury. 1.1895 gram. substance kept over H_2SO_4 in the dessicator; July 27th 1895. July 30th, wt. = 1.184 gram.; after a month's stay in the dessicator, the wt. was constant = 1.184 gram. 1.184 gram. substance gave 0.3485 gram. "free" Hg, = 29.43 per cent. "free" Hg; 0.246 gram. Hg_2Cl_2 from the *ous* salt in solution = 17.7 per cent. Hg.; and 0.422 gram. Hg_2Cl_2 from the *ic* salt = 30.27 per cent. Hg.

Preparation II.—1.2865 gram. substance gave 0.3957 gram. "free" Hg, = 30.76 per cent.; 0.25 gram. Hg_2Cl_2 from the *ous* salt = 16.5 per cent. Hg; and 0.4645 gram. Hg_2Cl_2 from the *ic* salt = 30.69 per cent. Hg. 1.224 gram. substance gave 0.3575 gram. "free" Hg, = 29.2 per cent.; 0.243 gram. Hg_2Cl_2 from the *ous* portion = 16.86 per cent. Hg; and 0.437 gram. Hg_2Cl_2 from the *ic* portion = 30.31 per cent. Hg.

Preparation III.—1.641 gram. substance gave 0.5025 gram. "free" Hg, = 30.62 per cent.; 0.348 gram. Hg_2Cl_2 from the *ous* salt = 17.8 per cent. Hg; and 0.5965 gram. HgS from the *ic* salt = 31.33 per cent. Hg.

The results are presented here in a tabulated form for convenience of reference.

	"Free" Mercury.	Mercury in the <i>ic</i> Salt.	Mercury in the <i>ous</i> Salt.	Total per cent. of Mercury.	
1.	31.5	} mean 78.56
2.	[29.43]	30.27	17.7	78.67	
3.	30.76	30.69	16.5	77.95	
4.	[29.2]	30.31	16.86	77.87	
5.	30.62	31.33	17.8	79.75	

The percentage of "free mercury" in analysis (2) and (4) respectively comes out too low. The cause of this has been already explained.

Whenever the mercury separates out as fine grey powder it is difficult to collect the whole of it into globules; during the decantation of the liquid a part of it is carried off, and during the process of boiling with hydrochloric acid to induce coagulation another portion is lost by volatilisation. As Fresenius himself remarks: "in general a little mercury is lost." In analysis (5) the percentage of mercury in the *ic* salt is a little too high, because this was estimated as HgS (see *ante* p. 4). It would be safe to take 30·7 as the percentage of mercury both in the "free" state as well as in the *ic* salt, and this number has been actually taken in calculating the percentage in (2) and (4).

B. *Estimation of Nitrogen.*

The salt was boiled with water and after separation of "free" mercury, the clear liquid was made up to a definite volume and generally 4 c.c. of it treated in the nitrometer. In the case of very dilute solutions of alkaline nitrites and nitrates it is generally the custom to take a larger volume of the liquid, evaporate it to dryness and then dissolve the residue in the minimum quantity (say 2 c.c.) of water. But unfortunately this could not be done in the present case, as thereby insoluble basic salts were formed. In dealing with small quantities any experimental errors would no doubt be highly magnified and thus tend to vitiate the result; but the method is one which admits of rigorous exactitude, as was proved by blank experiments with dilute solutions of protassium nitrate.*

Preparation IV. (a) Substance = 0·2554 gram.; Volume of solution = 65 c.c.

4 c.c. Sol. = 1·5 c.c. NO; $t = 33^{\circ}\text{C}$; $p = 760$ mean (mean of 4 concordant estimations).
Whence NO = 11·46 per cent.

(b) Substance = 2·008 gram.; Vol. of Sol. = 226 c.c.

4 c.c. Sol. = 3·5 c.c. NO (mean of 3 estimations); $t = 31^{\circ}\text{C}$; $p = 760$ m.m.

Whence NO = 11·87 per cent.

(c) Substance = 2·299 gram.; Vol. of Sol. = 234 c.c.

4 c.c. Sol. = 3·9 c.c. NO (mean of 4 estimations); $t = 32^{\circ}\text{C}$; $p = 760$ m.m.

Whence NO = 11·93 per cent.

* One who has made the estimation of nitrites and nitrates almost his life-long study testifies as regards the Crum-Frankland process, "that in the absence of organic matter and with proper manipulation in the shaking tube, the method is one of great accuracy, and capable of determining extremely small quantities of nitrates or nitrites." Warrington—Chem. Soc. Jour. 1879, page 387.

Evidence as to the salt being a nitrite pure and simple.

As the Crum-Frankland does not enable us to discriminate between the *nitrate* and the *nitrite*, use was made of the well known reaction between urea and nitrous acid.*

It was found that the solution of the *ous* and *ic* salt was only slowly and imperfectly acted upon by dilute sulphuric acid, it was therefore treated with pure caustic soda and warmed. In this way the nitrite was converted into an alkaline salt.

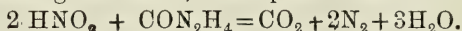
Substance = 0.7285 gram. ; Vol. of Sol. = 100 c.c.,

After absorption of CO₂ by strong lye :

4 c.c. sol. = 2.85 c.c. N	}	t = 32°C.
5 do. = 3.55 do.		
10 do. = 7.10 do.		

Whence NO = 11.7 per cent.

As the urea also gives up the whole of its nitrogen according to the equation given below, the experimental error is thus diminished by half.



Dunstan and Dymond's method of estimating nitrites was also applied; but in this case it is extremely difficult to prevent leakage of traces of air. The result in general was rather high.

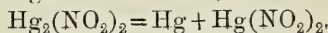
The mean of the several estimations of nitric oxide is 11.74.

Discussion of the Results and Theoretical Considerations.

The results accord well with the formula :

$\text{HgNO}_2 + 1/2 \text{H}_2\text{O} \dagger$		Theory.	Found.
Hg	= 200.00	78.43	78.55
{ NO	= 30.00	11.77	11.74
{ O	= 16.00	6.27	
1/2 H ₂ O	= 9.00	3.53	
	255.00	100.00	

On dilution with a sufficiently large quantity of water, the salt moreover undergoes dissociation; thus :



* For details of this process see "A gasometric method of determining nitrous acid," by P. F. Frankland. Chem. Soc. Jour. LIII, 364.

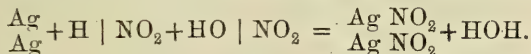
† While correcting the proofs I may as well mention here that the salt has the formula Hg₂NO₂. Since the memoir was presented to the Society, I have made repeated analyses of it, the mercury being estimated as sulphide, as phosphorous acid gives very low results in presence of nitrous acid. The percentage of "free" mercury has been found to be 31.41, that in the *ic* salt, 31.41 and that in the *ous* salt, 17.8 : total 80.62. Theory for Hg₂NO₂ requires 81.3.

The amount of mercury set free being equal to that contained in the *ic* salt, quantitative proof of which has been given above. The dissociation of mercurous nitrite is analogous to that of calomel:*



Diminution of pressure in one case playing the rôle of dilution in the other; nearly 22 per cent. of the salt, however, dissolves *as such*, and dilution has no further effect in increasing the proportion of dissociation. (*Vide* table, p. 4).

The present compound throws additional light on the action of nitric acid on the copper-mercury group of metals. It is now admitted by chemists that "in their relation to nitric acid metals must be divided into two classes." To the former belong those which produce ammonia and hydroxylamine from it; *e. g.* Tin, Zinc, Cadmium, Iron, Aluminium, Potassium, &c., while the latter includes Copper, Silver, Mercury and Bismuth. These seem to enter into direct union with the nitrogen of the acid, instead of displacing its hydrogen. The formation of the *nitro* compounds of the fatty series by V. Meyer's method lends additional support to this theory. This *nitronic* constitution of nitrous acid, as Divers puts it, also explains the advantage of red or yellow nitric acid in dissolving metals of the silver-mercury class.†



Indeed, the presence of nitrous acid seems to be *sine quâ non* for the dissolution of metals like silver, mercury, &c., as was first pointed out by Russell.‡ This chemist also showed that when silver dissolves in nitric acid, "silver *nitrite* is formed in quantity, partly in solution in the silver nitrite liquor, partly as crystals." The stability of silver nitrite in presence of strong nitric acid is noteworthy, as ordinary nitrites are decomposed even by the weakest acids. The *nitronic* nature of silver nitrite affords a ready explanation of this apparent anomaly.

Acworth and Armstrong in their classical researches found "that the amount of gas [NO] obtained by decomposing silver nitrite by nitric acid varies according to the strength of the acid, *being greater the weaker the acid*" (the italics are ours).....again "no amount of

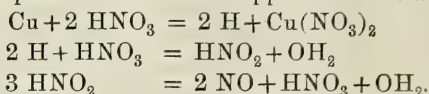
* Harris and V. Meyer's recent experiments fully bear out the conclusion arrived at by Odling years ago. See "Ueber den Molekularzustand des Calomedampfes" *Berichte*: 27 (1894) p. 1482.

† Divers: *Chem. Soc. Journ.* for 1883 *Trans.*, p. 443; also *ibid.* *Trans.* for 1885, p. 231.

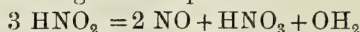
‡ "On the action of Hydrogen on Silver Nitrate," *Chem. Soc. Journ. Trans.* [2] xii. 3.

heating will effect this [decomposition] if the acid be concentrated."* Mercurous nitrite seems to behave exactly like silver nitrite.

The traces of nitrous acid, present in the yellow nitric acid, no doubt, start the reaction, but how to account for the continued formation of mercurous nitrite? For, this small quantity is soon used up according to the equation given above. There must be a parallel reaction going on to keep up the supply of nitrous acid. Acworth and Armstrong thus explain the action of copper on nitric acid.†

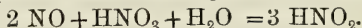


Adopting this view, the mercurous nitrite would continue to be formed for some time, and being insoluble in the menstruum, would be precipitated; whilst mercurous nitrate would remain in solution. The strength of the acid also would go on diminishing, till a time arrives when mercurous nitrite is no longer stable in this liquid, the nitrous acid decomposing according to the equation:



and Marignac's salt begins to be formed. The transformation of the nitrite into nitrate is however very slow, the process extending over weeks.

During the initial stages of the reaction the reverse change seems to take place; for, on the surface of the mercury somewhat brisk effervescence goes on, but proportionally very little nitric oxide escapes. During its upward ascent most part of it is absorbed, thus:—



A strong proof in favour of this view seems to be the fact that as soon as the superincumbent liquid is poured off, torrents of red fumes appear on the surface of mercury.‡

* On the Reduction of Nitric Acid, &c., Chem. Soc. Journ., Vol. LI. (1877), p. 54 *et seq.*

† Whether NO is formed through the agency of *nascent* hydrogen, or by the *direct* action of the metal on nitric acid must be left at present an open question. Cf. Deville: De l'état naissant, *Compt. Rend.*, 1870, LXX., 22, 550.

‡ Veley also arrives at this conclusion. "If the conditions are such that these metals [Copper, Mercury and Bismuth] dissolve, it would appear that the metallic nitrite is at first formed, together with nitric oxide. The former is decomposed by the excess of nitric acid to liberate nitrous acid, whilst the latter reduces the nitric acid to form a further quantity of nitrous acid."

"Eventually the net result is the product of two reverse chemical changes represented by the equations —

(1) $2 \text{NO} + \text{HNO}_3 + \text{H}_2\text{O} = 3 \text{HNO}_2.$

(2) $3 \text{HNO}_2 = 2 \text{NO} + \text{HNO}_3 + \text{H}_2\text{O}."$

Proc. Royal Soc. (1890), 48, page 458.

The place of mercury in the Periodic System would naturally justify the expectation that it would yield the *analogue* of silver nitrite, and the present compound is a realisation of it.

Although the compounds of monatomic mercury resemble the corresponding ones of silver, there is a sharp distinction between them. Silver never gives basic or hydrated salts, whilst the compounds of mercury with nitric or nitrous acids seem to be almost invariably basic or hydrated or both.

It has already been said that for purpose of analysis the first or second day's crop should be collected; after a longer time a granular mass of yellow rhombic tabular prisms (?) is obtained, which is rather richer in the percentage of mercury and at the same time much less stable. When this salt, after being dried on the porous tile, is kept in the bottle, it constantly evolves nitrous fumes.

Temperature also seems to have important bearing on the formation of the present salt. The ordinary temperature of the Laboratory in the summer season, 31° to 30°C ., seems to be very favourable for the growth of the needles.

The different mercurous nitrites and nitrates and *mercuric nitrite*, as also an attempt to prepare nitro-ethane with the aid of the compound now described, will form the subject of subsequent communications.

